imaginary parts of the function or the series. In particular *the series*

$$\sum n^{\rho-\frac{1}{2}} \cos\,(\alpha n \,\log\,n + 2\theta\pi n) \quad (\rho \geq 0) \tag{5.1}$$

is never convergent or summable for any value of θ, and is accordingly not a Fourier's series. We thus obtain a solution of what, in our former paper, we call Fatou's[9] problem which combines all the advantages of those given previously by Lusin,[9] Steinhaus,[9] and ourselves.

We can also obtain in this manner exceedingly elegant examples of continuous non-differentiable functions. Thus *the function*

$$f\,(\theta) = \sum \frac{\sin\,(\alpha n \,\log\,n + 2\theta\pi n)}{n^\beta} \quad (1 < \beta \leq \tfrac{3}{2}) \tag{5.2}$$

does not possess a finite differential coefficient for any value of θ.

[1] G. H. Hardy and J. E. Littlewood, Some problems of Diophantine approximation (i) *Proc. Fifth Int. Congress Math.*, Cambridge, **1**, 223–229 (1912); (ii) *Acta Math.*, **37**, 155–190 (1914); (iii) *Ibid.*, 193–238.

[2] G. H. Hardy, On certain oscillating series, *Quarterly J. Math.*, **38**, 269–288 (1907).

[3] G. H. Hardy, Weierstrass's non-differentiable function, *Trans. Amer. Math. Soc.*, **17**, 301–325, (1916).

[4] *l. c. supra* (1) (iii), p. 225.

[5] G. N. Watson, The singularities of functions defined by Taylor's series, *Quarterly J. Math.*, **42**, 41–53 (1911).

[6] G. H. Hardy: (i) A theorem concerning Taylor's series, *Ibid.*, **44**, 147–160 (1913); (ii) Note in addition to a theorem on Taylor's series, *Ibid.*, **45**, 77–84 (1914).

[7] Cf. E. Landau, Abschätzung der Koeffizientensumme einer Potenzreihe: (i) *Arch. Math. Physik*, ser. 3, **21**, 42–50 (1913); (ii) *Ibid.*, 250–255; (iii) *Ibid.*, **24**, 250–260 (1915).

[8] E. Landau, Uber die Anzahl der Gitterpunkte in gewissen Bereichen, *Göttinger Nachrichten*, 687–771 (p. 707), (1912).

[9] For references see p. 232 of our paper (1) (iii).

STERIC HINDRANCE AND THE EXISTENCE OF ODD MOLECULES (FREE RADICALS)

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The discovery of certain unpredicted facts in organic chemistry has led to the employment of the elusive phrase 'steric hindrance,' a phrase, however, which seems too vague in its significance to connote a real scientific theory. If a steric influence upon a chemical reaction be defined as one which is due to the room occupied by a large atom or group of atoms, such a definition leaves an opportunity for that kind of confusion, which is too frequently found in chemical literature, between

the factors that determine the speed of a reaction and those that determine the conditions of final equilibrium. In order to avoid such confusion it is necessary to distinguish between two possible types of steric influence:

1. A group of atoms, owing to its size and to its position in a molecule, may stand in the way so as to impede a reaction in which that molecule is involved. In other words, it may act merely to diminish the speed of such a reaction.

2. The space about a given atom may be so completely occupied by certain large groups of atoms, before the natural valence of the central atom is satisfied, that the entrance of another large group will be prevented; or if such a group occasionally enter, it will again be forced out through lack of room.

I think it will be admitted that these ideas, plausible as they are, should not be introduced into the already very complex body of chemical theory until phenomena are known which cannot be so well explained in other ways. In this paper I wish to discuss the so-called free radicals of organic chemistry, in the interpretation of which the term 'steric hindrance' has so often been employed, and to show that, in this case at least, another explanation can be offered which is more satisfactory in that it correlates a larger number of known phenomena.

After Gomberg, by treating triphenylmethyl chloride with metals, obtained a substance which he believed to contain triphenylmethyl, thus giving rise to one of the most interesting chapters of modern organic chemistry, it was at first commonly believed that by some other method a hexaphenylethane might be produced which would be stable and unreactive, and which would be formed from triphenylmethyl except for the retardation of this reaction by the first type of steric hindrance which I have just defined. We are now convinced that this is not the case. The later work of numerous investigators, which has been very completely reviewed by Gomberg[1] in his interesting summary, 'The Existence of Free Radicals,' has satisfactorily cleared an extremely intricate situation. A careful study of the work of these authors must, I believe, lead to the acceptance of the following perfectly definite conclusions concerning the class of hexa-arylethanes, of which hexaphenylethane is the simplest example.

I. The hexa-arylethanes, aside from the irreversible processes of intramolecular rearrangement and autoxidation to which they are subject and which we shall not further consider, exist in a state of tautomeric equilibrium between quinoid forms and the benzoid form which represents the simple substituted ethane. As in most similar cases the

equilibrium is shifted in favor of the quinoid type in polar solvents, and in a very polar solvent such as SO_2 the molecules may dissociate into positive and negative ions of which the former (and probably the latter also) is largely in the quinoid form.

The recognition of the existence of the quinoid form is indispensable to an understanding of numerous reactions which characterize the hexa-arylethanes, but since we are here concerned with that part of the substance which remains in the benzoid form we may proceed at once to the next conclusion.

II. In nonpolar solvents such as benzene the substituted ethanes exist chiefly in the benzoid form and are to a greater or less extent dissociated into the triarylmethyls. The undissociated part is colorless. The product of dissociation, though colored, has also the benzoid form.

The fact of dissociation has been abundantly demonstrated. The mere fact that the equilibrium between colorless and colored forms changes in favor of the latter with increasing dilution[2] shows that the change from colorless to colored is attended by an increase in the number of molecules. Measurements of the degree of dissociation, whether through molecular weight determinations or by colorimetric methods, show that while the parent substance, hexaphenylethane, is at ordinary temperatures only to a few per cent dissociated, the dissociation is nearly complete in the case of some other aryl derivatives. Schmidlin[3] has shown that the process of dissociation is not instantaneous but requires a short though appreciable time, and hence he was able to show that it is the colored substance which reacts rapidly with oxygen or iodine, thus exhibiting the characteristics of a free radical. Indeed it might be possible under favorable circumstances to obtain the degree of dissociation in a new way by rapid titration of the colored substance against atmospheric oxygen.

Gomberg has hesitated to adopt the conclusion that the colored triarylmethyls retain the benzoid form, on the ground that there is no analogy to support the assumption that a colored substance could be formed by the mere dissociation of a colorless substance such as the substituted ethane. It is true there is no analogy in organic chemistry except among these very compounds of trivalent carbon, and the corresponding compounds of bivalent and quadrivalent nitrogen which have been investigated with great perspicuity by Wieland and his collaborators. If, however, we examine the whole field of chemistry, we see that triphenylmethyl belongs to a class of substances which are almost invariably colored and which are typified by NO_2 which, like

triphenylmethyl, associates at low temperature or high concentration to form the colorless double molecule. They are the substances which possess what I have called, in a recent paper,[4] *odd molecules*.

I will review briefly the significance of this term. If we assume that every neutral atom possesses in its outer shell a number of electrons corresponding to the ordinal number of the element's group in the periodic system, for example, H, 1; C, 4; N, 5; O, 6; Cl, 7, then in almost all compounds there is an even number of such electrons. Those few substances which possess an odd or unpaired electron are said to have odd molecules. Thus sodium in the state of vapor has 1, monatomic iodine has 7, NO_2 has 17, ClO_2 has 19, $(C_6H_5)_3C$ has 91, $(C_6H_5)_2N$ has 63, and $(C_6H_5)_2NO$ has 69. Since an unpaired electron is always held in the molecule by weak constraints, it is usually capable of oscillating with so low a characteristic frequency as to absorb visible light. This absorption, moreover, involving only a single electron, might be expected to be of the simplest possible character.

In fact it has been shown by Wieland[5] that several substances of this type, with odd molecules, have very characteristic absorption spectra possessing ordinarily a single absorption band. Thus the spectrum not only of $(C_6H_5)_2NO$ but also of the triarylmethyls is like that of NO_2 and by no means resembles that of such quinoid substances as triphenylmethyl ion. There seems therefore every reason to believe that triphenylmethyl is colored not because it assumes the quinoid form but because it possesses an odd electron which, as in every other known substance of this class except NO, has a sufficiently low natural frequency to absorb visible light.

But whether or not this point be admitted, the fact that equilibrium is rapidly established between the ethanes and their corresponding methyls shows conclusively the non-existence of the first type of steric hindrance. Instead of a retardation due to the large groups we find a reaction velocity which, among organic compounds, is exceptionally high.

Therefore in the discussion of this type of reaction the term, steric hindrance, tacitly came to be employed in the second sense, implying a crowding out of large groups by other large groups, and this view seemed to be favored by the discovery by Schlenk that the degree of dissociation of the hexarylethanes ordinarily increases with increasing complexity of the substituted aryl groups.
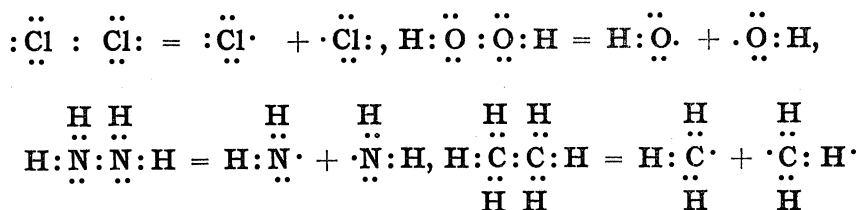
In order to obtain a comprehensive view let us consider four substances which in the light of the periodic system must in certain re-

spects be regarded as analogous, namely, Cl—Cl, HO—OH, H_2N—NH_2, H_3C—CH_3. The chlorine molecule acquiring rotational energy due to temperature has a certain tendency, through centrifugal force, to break at the bond of union into monatomic molecules. The molecule of bromine with its heavier atoms has, especially in view of modern quantum theory, a higher moment of momentum and is therefore dissociated to a higher degree, while iodine with its still heavier atoms is to a large degree dissociated at easily attainable temperatures. No one has suggested that this dissociation of iodine vapor is due to steric hindrance. The volume occupied by an atom is at best a most indefinite conception, but the atomic volume commonly attributed to iodine is not greater than that attributed to bromine or chlorine. It is doubtless the mass of the iodine atom which is chiefly responsible for its greater dissociation.

Since diatomic iodine dissociates to give nul-valent iodine we may expect to find a properly substituted hydrogen peroxide dissociate to give a compound of univalent oxygen, as the substituted hydrazines and ethanes have been found to give compounds of bivalent nitrogen and trivalent carbon. Both in hydrazine and in ethane it is the substitution of heavy groups which causes appreciable dissociation. Thus pentaphenylethane does not dissociate sufficiently to show the properties of a free radical below 180°, where it absorbs oxygen readily.[6] Hexaphenylethane is at room temperature dissociated to the extent of several per cent. The successive substitution of phenyl by biphenyl[7] increases the dissociation regularly. Now it is possible, but not obvious, that biphenyl occupies more space immediately about the methyl carbon than phenyl does. It certainly seems better to assume that by increasing the mass of the group and thus increasing the centrifugal force at the central bond, it produces a greater dissociation.

Another interesting illustration of the effect of the mass of the substituent upon dissociation is afforded by the interesting substance obtained by Wieland in which one oxygen of NO_2 is replaced by two phenyl groups. While NO_2 is largely associated even at ordinary temperatures $(C_6H_5)_2NO$ remains monomolecular even at the lowest temperature obtainable with solid CO_2 and ether.

The relation between nul-valent chlorine, univalent oxygen, bivalent nitrogen and trivalent carbon is more readily visualized if we express the equations of dissociation in the symbols of my previous paper:

$$\overset{..}{:}\text{Cl}\overset{..}{:}\text{Cl}\overset{..}{:} = \overset{..}{:}\text{Cl}\cdot + \cdot\overset{..}{\underset{..}{\text{Cl}}}: , \quad \text{H}\overset{..}{:}\underset{..}{\text{O}}\overset{..}{:}\underset{..}{\text{O}}\text{:H} = \text{H}\overset{..}{:}\underset{..}{\text{O}}\cdot + \cdot\overset{..}{\underset{..}{\text{O}}}\text{:H},$$

$$\overset{\text{H}\quad\text{H}}{\underset{\overset{..}{\underset{..}{\text{H}:\text{N}:\text{N}:\text{H}}}}{}} = \text{H}\overset{..}{:}\underset{..}{\text{N}}\cdot + \cdot\overset{..}{\underset{..}{\text{N}}}\text{:H}, \quad \overset{\text{H}\quad\text{H}}{\underset{\text{H}\quad\text{H}}{\text{H}:\text{C}:\text{C}:\text{H}}} = \overset{\text{H}}{\underset{\text{H}}{\text{H}:\text{C}\cdot}} + \overset{\text{H}}{\underset{\text{H}}{\cdot\text{C}:\text{H}\cdot}}$$

The symbols in heavy type represent the atomic kernels, while the dots represent the electrons of the outer shells. It is the odd electrons that gives the free radicals color and high reactivity. It will be understood that the particular substances used for illustration are dissociated only to an extremely small degree; only upon substitution of heavier radicals will the dissociation be appreciable at ordinary temperatures.

In emphasizing the effect of mass and thus of centrifugal force in breaking a chemical bond we must not forget, however, that this is only one of the two main factors that determine the stability of a molecule. The other factor is the strength of the constraints which constitute the bond itself. (Electrochemical influences which are so frequently important do not concern us here since we are considering a bond symmetrically placed between two identical radicals.) I have pointed out, in the paper already cited, that the bond between two carbon atoms is weakened when either atom has a double bond or is attached directly to an atom with a double bond. Thus the great change produced by the substitution of phenyl for hydrogen or alkyl is due to both increasing mass and a weakened bond. If the phenyl groups in hexaphenylethane are replaced by the somewhat heavier benzyl groups the dissociation will nevertheless be diminished, since the benzyl will not aid in weakening the central bond. On the other hand there are radicals which cause a still greater weakening of the central bond than the phenyl group. Thus Gomberg has shown that the linking of two of the phenyl groups of triphenylmethyl by an atom of oxygen in the ortho positions greatly increases the percentage of free radical.

The odd molecules produced by the thermal dissociation of the substances here considered may combine not only with their like but with other free radicals to produce mixed types. Thus the reaction $(Ar)_2N - N(Ar)_2 + (Ar)_3C - C(Ar)_3 = 2(Ar)_3C - N(Ar)_2$ is analogous to the reaction $(Ar)_3C - C(Ar)_3 + I_2 = 2(Ar)_3C - I$. Wieland[8] has found a very interesting reversible reaction $(C_6H_5)_3C - C(C_6H_5)_3 + (C_6H_5)_2N - N(C_6H_5)_2 = 2(C_6H_5)_3C - N(C_6H_5)_2.$

By some reaction of this type, if proper protection against intramolecular rearrangement be provided, we may predict that a di-aryl substituted hydrogen peroxide will be prepared, which in turn will dissociate into mono-aryl oxide, ArO, the odd molecule, or free radical, of univalent oxygen. Such a peroxide would probably be less dissociated than the similarly substituted hydrazine, just as the latter is less dissociated than the corresponding ethane.

[1] Gomberg, *J. Amer. Chem. Soc.*, **38**, 770 (1916).

[2] Piccard, *Liebig's Ann. Chem.*, **381**, 347 (1911).

[3] Schmidlin, *Ber. D. Chem. Ges.*, **41**, 2471 (1908).

[4] Lewis, *J. Amer. Chem. Soc.*, **38**, 770 (1916).

[5] Wieland and Offenbecher, *Ber. D. Chem. Ges.*, **47**, 2111 (1914); Meyer and Wieland, *Ibid.*, **44**, 2557 (1911).

[6] Chichibabin, *Ibid.*, **40**, 367 (1907).

[7] Schlenk, Weickel and Herzenstein, *Liebig's Ann. Chem.*, **372**, 1 (1910).

[8] Wieland, *Ibid.*, **381**, 200 (1911).

NEWTON'S METHOD IN GENERAL ANALYSIS

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The present paper is essentially an extension of the methods and results given by Dean H. B. Fine, On Newton's Method of Approximation,[1] and the results there obtained need not be explained here.

An illustration of some general notions.—As might be expected, Newton's Method is of very wide application and may be used, for example in the following three cases to find a real 'root' of the real functionelle $F[x(s)]$ where F has the property that in a certain domain, and for every $x(s)$ and $x(s) + h(s)$ in this domain, there exist functionelles F_1 and F_2 for which

$$F[x(s)+h(s)] \equiv F[x(s)] + \int_0^1 F_1[x(s), r]h(r)dr + \int_0^1 \int_0^1 \tfrac{1}{2} F_2[\xi(s), r_1, r_2] h(r_1) h(r_2) dr_1 dr_2, \qquad (A)$$

(1) where $\xi(s)$ is such that $\max_s | \xi(s) - x(s) | \leqq \max_s | h(s) |$ and $\max_s | x(s) + h(s) - \xi(s) | \leqq \max_s | h(s) |$, if by 'max' is meant the maximum as s varies, and by a 'root' of the above equation is meant a function $x(s)$, such that $\max_s | F[x(s)] | = 0$; or (2) where $\xi(s)$ is such that $\sqrt{\int_0^1 [\xi(r) - x(r)]^2 dr} \leqq \sqrt{\int_0^1 h^2(r) dr}$ and $\sqrt{\int_0^1 [x(r) + h(r) - \xi(r)]^2 dr} \leqq \sqrt{\int_0^1 h^2(r) dr}$, and by a 'root' is meant a function $x(s)$, such that $\sqrt{\int_0^1 F[x(r)]^2 dr} = 0$; or (3), where $\xi(s)$ is such that $\int_0^1 | \xi(r) - x(r) | dr \leqq$